

## PALLADIUM (Pd).

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*(Read April 7, 1904.)*

Although palladium belongs to the platinum group of metals, it is in some respects nearly related also to silver, its atomic weight and specific gravity being respectively about 107 and 11.4, while the corresponding figures for silver are 108 and 10.5. In its high melting point, however, of 1500° C., it approaches more nearly to platinum which melts at 1750° C., and in color its grayish-white resembles the color of platinum more nearly than that of silver.

Palladium has long been known to occur native in company with platinum, and also alloyed with gold in the Brazilian mineral porpezite which contains about 5 to 10 per cent. of it. That it occurs in notable quantity in the nickeliferous pyrrhotite of Canada is an important recent observation.

Both platinum and palladium probably exist to a greater or less extent in all the many deposits of nickeliferous pyrrhotite throughout the world; certainly in those of Norway and Sweden, and particularly in every one of the numerous deposits of that mineral which are found in the Laurentian and Huronian rocks surrounding the little town Sudbury, in the province of Ontario, Canada. The quantity, however, is extremely small, varying from a mere trace to one or more ounces per ton; the average for each metal being about one-hundredth of an ounce per ton of ore, platinum and palladium usually being present in approximately equal parts.

Yet, though known to exist in many parts of the world, palladium has not been diligently sought for, because there was until recently no considerable demand for it; the reworking of platiniferous residues from the mints of several countries having supplied most of that which appeared in commerce. The prevailing scarcity of platinum is now directing attention to palladium as a practicable substitute for some purposes.

The nickeliferous pyrrhotite deposits of the Sudbury region have recently become the most important source of nickel in the world and appear certain to continue so for many years, having quite surpassed in yield the great nickel-silicate ores of New Caledonia which come next in rank. In these Canadian ores, silver, gold, platinum, iridium and rhodium occur as well as palladium; all in very minute quantities—palladium as above mentioned to the extent of about .01 oz. per ton.

The form in which palladium there occurs has not been detected, for owing to its minute quantity and the consequent difficulty of isolating it, none has yet been directly observed in any ore of that region; since, however, platinum occurs there as arsenide in the interesting mineral sperrylite ( $\text{Pt,As}_2$ ), palladium may exist in similar combination, though none has been observed in any specimen of sperrylite that has been examined. Prof. Horace L. Wells indeed notes a trace of palladium in sperrylite, but this has not I think been confirmed in any of the careful analyses of other good chemists.

In the one mine where platinum-arsenide has been found, Prof. Wells says it occurs in small pockets of decomposed rock at the contact of ore and rock, these pockets being filled with loose gravelly material. It was in the metallic sparkles of that sandy stuff where the sun's rays struck it that Mr. Sperry first noticed what proved to be platinum-arsenide—a substance till then unknown.

Ten years ago, when I visited the mine in question, the Vermillion Mine, I observed, upon the surface of the ground where the ore had been dumped, a moderate quantity of sand which appeared to have resulted from the disintegration and metasomatism of ore by atmospheric penetration, and this seems to afford a plausible explanation how palladium-arsenide might have been present in the ore with platinum-arsenide and yet no palladium be now detectible in the Sperrylite; for the greater oxidability of palladium may have led to the conversion of its arsenide into arseniate, afterward leached away by the percolating water.

Though the Vermillion Mine is not at present in operation, it affords, as above stated, the only indication we have as to the probable condition of both platinum and palladium in the ores of other mines in that region from which those metals are extracted, though neither metal has been directly observed in any of those other mines.

The ore from those other mines is not simply nickeliferous pyrrhotite, but is also to a considerable extent chalcopyrite, yielding therefore much copper, as well as nickel and minute proportions of the above-named precious metals. The ores of the various mines in the Sudbury region may be reckoned as containing  $1\frac{1}{2}$  to 8 per cent. of nickel (some small quantities even 30 to 40 per cent.) and 1 to 4 per cent. of copper.

Those ores are roasted in open heaps and then smelted into matte containing by average about 30 per cent. of nickel and copper,

and containing also practically all of the precious metals which the ores carried.

After further roasting and smelting, the concentrated matte is treated for separation of copper from nickel, which is effected by repeated melting with nitre cake and coke in cupola furnaces. The coke converts the nitre cake into sodium sulphide; when the charge is run out of the furnace and cooled it separates easily into two parts, the bottoms containing practically all the nickel, the tops consisting of sodium sulphide and copper sulphide; the gold and silver going with the tops, the platinum-group metals going with the bottoms.

In the refining processes that follow, palladium is obtained as a slime, carrying about a thousand times as much palladium proportionally as did the original ore, carrying also the other platinum-group metals, and the gold and silver.

This palladium-bearing slime is melted and refined in a small reverberatory furnace, from which it is ladled out into cold water, forming shot which are charged into small leaden towers, into the top of which hot dilute sulphuric acid is run. Palladium and the other precious metals being electro-negative to the base metals, a galvanic action now takes place in which nickel, copper and iron dissolve rapidly, leaving palladium in a black mud containing two per cent. or more of that metal. If this residue still contains much copper, that is mostly eliminated by further treatment with hot sulphuric acid until the stuff contains about 25 per cent. of palladium, when it is treated with aqua-regia, thus dissolving all the platinum, palladium and gold.

From this solution platinum is precipitated by ammonium chloride, the palladium in the filtrate is electrolytically precipitated with a platinum anode, appearing as a dull gray metal which is hard and brittle, peeling off easily from the cathode. It is then dried and ignited in a reducing atmosphere, when it takes great brilliancy and becomes very soft and pliable, capable of being worked into any ordinary form. I have, for instance, a remarkably nice teaspoon made of it.

If air is not completely excluded during ignition the palladium will oxidize on the surface taking most beautiful colorations of pink and green. When prepared as above stated palladium is almost absolutely pure, but for occasional traces of copper and iron.

I purposely refrain from giving all details of the various stages of

the processes by which pure palladium is finally attained, but enough is stated to show that a complete working system is established, requiring, of course, delicacy of perception and dexterous manipulation, yet yielding at last a beautiful substance capable of sundry uses, which are undeveloped only because no regular supply could hitherto be counted on. The steady production of palladium by the Orford Copper Co. is now more than 3000 ounces annually, from approximately 300,000 tons of Canadian ores treated. It is obvious that only as a by-product in the working of very great quantities of ore can palladium be produced as here stated.

Besides having so very high a melting point, and being at the same time both hard, ductile and malleable, palladium is so absolutely non-corrodible that a sheet of it may hang for a long time in a laboratory exposed to chlorine and hydrogen-sulphide gases without losing its polish or tarnishing.

The wonderful occlusion or absorption of hydrogen by palladium deserves special attention and invites further study.

The volume of hydrogen thus absorbed varies greatly under different circumstances, and has been variously stated by different observers. According to Graham (*Phil. Mag.*, [4] 32, 401, 503):

Fused palladium at 200°	absorbs	68 volumes.
Finely divided palladium at 200°	"	686 "
Sheet palladium at ordinary temperatures (after ignition)	"	376 "
" " " 90° to 97°	"	643 "
" " " 245°	"	526 "

In Poggendorff's *Annalen* for 1869, Graham describes experiments in which 900 volumes were absorbed.

The greatest absorption observed before the experiments of McElfresh (mentioned below) was shown by electrolytically precipitated palladium; the maximum being 982.14 volumes of hydrogen.

Schmidt (*Ann. Physik.*, iv, 13,747), *J. Chem. Soc.*, 85, 86, 312 (1904), finds that the volume of hydrogen absorbed by palladium increases with the fall of temperature to about 140°; below this he finds concordant results. From 140° to 300° the absorption curve approaches a straight line. Absorption, and also diffusion, increases with pressure as well as with temperature.

Hoitsema (*Zeit. physikal. Chemie.*, 1895, 17, 1), *J. L. C. S.*, 78, 11,388 (1895) examines the hypothesis of Troost and Hauteville, that in the absorption of H by Pd a compound is formed repre-

sented by  $\text{Pd}_2\text{H}$ , but he does not agree with those authors. Debray thought the compound  $\text{Pd}_4\text{H}_2$  was formed. Why should a chemical formula be sought for the compound of palladium and hydrogen since they combine together in practically all proportions, thus indicating it to be a simple alloy?

McElfresh (*Proc. Am. Acad. Arts and Sciences*, vol. xxxix, No. 14, Jan., 1904), examining critically the influence of occluded hydrogen upon the electrical resistance of palladium, finds that resistance to increase constantly, but not at a uniform rate, as the occluded hydrogen increases; the maximum increase of the resistance being 68 per cent. when 1030 volumes were occluded. This absorption, reached by continuous exposure for 30 hours, is the highest yet observed and probably indicates complete saturation.

McElfresh considered Knott's method (*Proc. Roy. Soc. Edin.*, vol. xii, 1882, 1883) of determining the amount of occlusion, by measuring the increase in weight of the palladium treated, to be incapable of accuracy; he was also dissatisfied with the results obtained with imperfect apparatus by supplying to palladium a measured quantity of electrolytically produced hydrogen and deducting therefrom the quantity remaining after various periods of absorption. He therefore avoided the error inherent in such apparatus by using in this latter method ingenious apparatus of his own devising, thus reaching conclusions which appear quite reliable.

It is remarkable that Richter's *Chemistry*, as translated by Edgar F. Smith, states (p. 46) that the conductivity of palladium for both heat and electricity is little affected by its occlusion of hydrogen.

As for the discharge of occluded hydrogen from palladium, Graham states that "the gas exhibits no disposition to leave the metal and escape into a vacuum at the temperature of its absorption." Edgar F. Smith informs me that he finds charged palladium immersed in water at  $160^\circ$  to give off hydrogen with freedom comparable to the escape of carbonic acid from soda water.

Baskerville informs me that, in examining palladium for radio-activity, he found none in either of the two forms I sent him at his request for that purpose—namely, electrolytically deposited scale such as mentioned above in this paper, and similar scale which had been fused into a large button. But when he examined the same specimens after charging them in a finely divided state with hydrogen, he found slight indications of radio-activity in the first, but none in the second. He therefore asks whether, during the electro-deposition, a tension might have accumulated which



appeared afterward as beta-rays. Query: If so, why should the electro-scale require charging with hydrogen to enable it to indicate radio-activity?

Sir William Ramsay, to whom I mentioned this experiment and surmise, suggested the possibility that the original ore might have contained a trace of radium, which persisted with the palladium until the final fusion vaporized it or passed it to the slag.

Among the chemical characteristics of palladium may be mentioned these, not of course as novelties but as practically useful:

1. It is completely precipitated from an acid solution as sulphide by hydrogen-sulphide.

2. It is thrown down as a black precipitate from even a dilute solution by potassium-iodide. This very sensitive reaction is important in practical treatment of material containing palladium.

3. It is precipitated by mercury-cyanide as white slimy palladium-cyanide: a property useful for quantitative determination in laboratory.

Among the uses hitherto of palladium are:

1. For the mechanism of delicate instruments such as chronometers, and for verniers, etc., of astronomical instruments.

2. For surgical instruments.

3. For plating searchlight mirrors. Why not for the mirrors of reflecting telescopes?

4. For alloying with silver to make dental plates, etc., instead of the  $\frac{2}{3}$  silver,  $\frac{1}{3}$  platinum hitherto used in Europe. Also as palladium amalgam for fillings in cavities of teeth.<sup>1</sup>

Other uses will naturally arise as men's minds are turned toward this metal, which, while in many respects equal to platinum, sells for no more than the price by weight of that metal, and of course

<sup>1</sup> Palladium amalgam has been used to but very small extent for tooth fillings, though well adapted for that use except for its dark color, arising apparently from palladium black being used to form the amalgam, which is made by the dentist at the moment he wishes to use it, by triturating palladium black with mercury. That darkness of color might probably be obviated by using fine palladium filings instead of palladium black.

Dr. Joseph Pettit, a careful observer, told me that he had found this amalgam so made to become too hot to be comfortably held in the hand. Dr. W. Storer How, of the S. S. White Dental Co., informed me that he had noticed some warmth evolved in the making of the amalgam. I observed very little heat, no more in fact than I thought referable to the friction of trituration.

therefore for much less than that by bulk; the specific gravity of platinum being variously stated as 17 to 19, and that of palladium as 11.4 to 11.8.

It would seem that palladium might be useful under some circumstances for resistance wire.

I conclude by remarking that, in the several reports by the Canadian Government upon the metallic and mineral resources of "The Dominion," palladium is never mentioned; not even in the report for 1904.

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*Stated Meeting, April 15, 1904.*

President SMITH in the Chair.

Prof. Edward Potts Cheyney and Dr. Harvey W. Wiley, newly elected members, were presented to the Chair, and took their seats in the Society.

Letters accepting membership were read from:

President Roosevelt, Washington, D. C.

Prof. Maurice Bloomfield, Baltimore.

Prof. Henry Pickering Bowditch, Jamaica Plain, Mass.

Prof. Edward Potts Cheyney, Philadelphia.

Prof. Russell H. Chittenden, New Haven.

Prof. Frank Wigglesworth Clarke, Washington.

Prof. Kuno Francke, Cambridge, Mass.

Prof. Edward Leamington Nichols, Ithaca.

Prof. Samuel W. Stratton, Washington.

Dr. Harvey W. Wiley, Washington.

Prof. C. L. Doolittle discussed a letter from Mr. Germers on the Aurora Borealis, and explained the phenomena referred to therein.

The following papers were read:

"The Trail of the Golden Dragon," by Dr. George B. Gordon.

"Views of Old Philadelphia," by Mr. Julius F. Sachse.